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54 Epoxidation process using titanium-rich silicalite catalysts.

57 Olefins are epoxidized by hydrogen peroxide in the presence of a crystalline titanium silicalite zeolite catalyst having a Si:Ti molar ratio in the lattice framework of from 8:1 to 23:1. High yields of epoxides with minimal non-selective loss of either hydrogen peroxide or olefin are realized.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 3310 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to date	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Y	LA CHIMICA & L'INDUSTRIA vol. 72, no. 7, 1990, MILAN (IT) pages 610 - 616 U. ROMANO ET AL. 'Selective oxidation with Ti-silicalite' * the whole document *	1-18	C07D301/12
D,Y	JOURNAL OF CATALYSIS vol. 130, 1991, NEW-YORK (USA) pages 1 - 8 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. I. Synthesis and Characterization of Titanium-Rich Zeolites with MFI Structure' * the whole document, particularly paragraph bridging pages 6 and 7*	1-18	
Y	JOURNAL OF CATALYSIS vol. 131, 1991, NEW-YORK (USA) pages 294 - 297 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. II. Hydroxylation of Phenol with Hydrogen Peroxide over TS-1 Zeolites' * the whole document, particularly page 294, paragraph bridging left- and right-hand columns	1-18	
Y	JOURNAL OF CATALYSIS vol. 131, 1991, NEW-YORK (USA) pages 394 - 400 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. III. Ammoxidation of Cyclohexanone' * the whole document, particularly paragraph bridging pages 395 and 396	1-18	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 January 1994	Examiner Allard, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		Y : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons * : member of the same patent family, corresponding document	

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# EUROPEAN SEARCH REPORT

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EP 93 30 3310

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 8)
E	EP-A-0 568 337 (ARCO CHEMICAL TECHNOLOGY) 3 November 1993 * the whole document, particularly page 6, lines 29-35 -----	1-18	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 8)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 January 1994	Examiner Allard, M
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>*****  A : member of the same patent family, corresponding document</p>			

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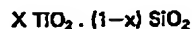
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(54) A process for the epoxidation of olefinic compounds.

(57) A process for the epoxidation of olefinic compounds comprising reacting said compounds with hydrogen peroxide introduced as such or produced by substances under the reaction conditions, in the presence of synthetic zeolites containing titanium atoms corresponding to the general formula:



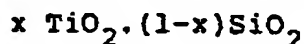
wherein x is in the range of from about 0.0001 to about 0.04, and optionally, in presence of one or more solvents, at a temperature in the range of from about 0 to about 150°C. and at a pressure of from about 1 to about 100 atm. The synthetic zeolites are treated with alkaline substances before and/or during their use in the reaction, or alternatively the synthetic zeolites are acid neutralized with a compound such as  $X\text{-Si-(R)}_3$  where X is selected from Cl, Br, I,  $\text{CH}_3\text{CON-Si-(CH}_3)_2$ ,  $\text{CF}_3\text{COON-Si-(CH}_3)_2$ ,  $\text{(R)}_3\text{-Si-NH}$ , and an imidazolyl group wherein R is selected from an alkyl, aryl or alkylaryl group.

### FIELD OF THE INVENTION

The present invention is directed to a process for the epoxidation of olefinic compounds with hydrogen peroxide introduced as such or produced by substances under the reaction conditions, in presence of synthetic zeolites containing titanium atoms, wherein the synthetic zeolites are [acid]neutralized < as to their acidity>.

### BACKGROUND OF THE INVENTION

European Patent Application No. 100119 discloses a process for the epoxidation of olefinic compounds, starting from olefins and hydrogen peroxide or substances which can produce hydrogen peroxide under the reaction conditions, wherein the catalyst is a synthetic zeolite containing titanium atoms (titanium-silicalite) corresponding to the general formula:



wherein x is in the range of from 0.0001 to 0.04. The catalyst is chosen from among catalyst compositions having the following molar ratios of reactants:

<u>Molar Ratios of Reactants</u>			<u>Preferred Molar Ratios</u>
25	$\text{SiO}_2/\text{TiO}_2$	5-200	35-65
	$\text{OH}^-/\text{SiO}_2$	0.1-1.0	0.3-0.6
	$\text{H}_2\text{O}/\text{SiO}_2$	20-200	60-100
	$\text{Me}/\text{SiO}_2$	0.0-0.5	0
	$\text{RN}^+/\text{SiO}_2$	0.1-2.0	0.4-1.0

wherein  $\text{RN}^+$  represents an organic nitrogen cation derived from the organic base utilized for the preparation of titanium-silicalite (TS-1). Me is an alkaline ion, preferably chosen from among Na or K.

The final TS-1 product is a composition having the formula  $x \text{TiO}_2 \cdot (1-x) \text{SiO}_2$  wherein x is in the range of from 0.0001 to 0.04, preferably from 0.01 to 0.025.

TS-1 is silicalite type product wherein titanium atoms vicariously replace the silicon atoms. A further and more precise identification of the titanium-silicalite which is used as a catalyst is set forth in said European patent application and in Belgian Patent No. 886812.

The titanium-silicalite catalyst may be utilized in the expoxidation reaction as a dust or preferably in the form of granules having a particle size of from 5 to 1000  $\mu\text{m}$  wherein the granules are made of zeolitic crystals bound by a suitable inorganic binder, preferably oligomeric silica.

It has been observed that in the synthesis of epoxidized compounds derived from olefins and hydrogen peroxide with said catalysts in a protic medium (such as water, alcohol and mixtures thereof), selectivity of the desired epoxide is generally very high. Yet some amount of by-products from solvolysis is always present, especially when working at high temperatures. This results in increased costs because of the lower yield of the epoxide and because of the need to separate the by-products from the reaction.

It has surprisingly been found that it is possible to significantly reduce the amount of the aforesaid undesirable by-products by treating the catalyst prior to the reaction or during the reaction with suitable acid neutralizing agents to neutralize acid groups which are on the catalyst surface. The catalyst can also be treated with a substance which can neutralize catalyst acidity using an inert group bound to a polar group which is easily displaced by reaction with  $\text{SiOH}$ .

The acidity of non-treated titanium-silicalite is already very low which is due to the presence of some SiOH groups, especially on the outer surface of the crystals or in the lattice defects. However, the  
5 presence of even a small number of acid groups results in the production of unacceptable amounts of by-products due to the solvolysis reaction described above.

#### SUMMARY OF THE INVENTION

10 The process of the epoxidation of olefinic compounds in accordance with the present invention comprises reacting in a reaction zone one or more olefinic compounds with hydrogen peroxide or substances which produce hydrogen peroxide under the reaction  
15 conditions, in presence of a catalyst comprised of a synthetic zeolite (titanium-silicalite), wherein the catalyst is, prior to the epoxidation reaction, neutralized as to its acidity by a compound of the formula  $X-Si-(R)_3$  wherein X is selected from Cl, Br, I,  $CH_3COON-Si-(CH_3)_3$ ,  
20  $CF_3COON-Si-(CH_3)_3$ ,  $(R)_3-Si-NH$ , and an imidazolyl group, wherein R is an alkyl, aryl or alkaryl group wherein the alkyl group has from 1 to 4 carbon atoms.

Catalyst neutralization may also be accomplished  
25 before and/or during the reaction, with basic substances which are water soluble. Such basic substances may be chosen from among strong bases, such as NaOH, KOH, and weak bases such as  $NH_4OH$ ,  $Na_2CO_3$ ,  $NaHCO_3$ ,  $Na_2HPO_4$  and analogous potassium and lithium salts including  $K_2CO_3$ ,  
30  $Li_2CO_3$ ,  $KHCO_3$ ,  $LiHCO_3$  and  $K_2HPO_4$ , alkaline and/or alkaline-earth salts of carboxylic acids having from 1 to 10 carbon atoms and alkaline and/or alkaline earth alcoholates, having from 1 to 10 carbon atoms.

35 In a batchwise epoxidation reaction,

neutralization of the catalyst with basic substances, which are water soluble, is carried out by forming a slurry of the catalyst in a diluted solution of the neutralizing agent chosen among those mentioned above and stirring the slurry at a temperature of from about room temperature to about 100°C. for a few minutes. The catalyst is then removed and thoroughly washed to completely remove excess base. After drying, the catalyst is utilized for the epoxidation of the olefin, with surprisingly high selectivity to epoxide. In the event the epoxidation reaction is performed in a continuous flow (fixed bed reactor, CSTR reactor, i.e., continuous flow stirred tank reactor), it is sufficient to add to the hydrogen peroxide feed from about 0.0001 to about 0.1% by weight of a neutralizing agent which is soluble in the medium and weakly basic, (e.g.,  $\text{CH}_3\text{COONa}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{CO}_3$  and the like) in order to prevent deterioration of the catalyst over time. In this way, it is possible to prevent indefinitely the catalyst from initiating the undesirable solvolysis by product formation reaction. The amount of the neutralizing agent which is employed depends on the nature of the reaction medium, the space velocity, and the temperature.

Alternatively, neutralization of the catalyst is conducted by reacting the compounds of the general formula  $(\text{X-Si}(\text{R})_3)$  with the titanium-silicalite.

The reaction may be carried out in an inert solvent such as acetonitrile, chloroform, pyridine and dioxane and the like with or without an organic base such as pyridine or at least one tertiary amine. In accordance with this procedure, it is possible to transform all of the  $\text{SiOH}$  groups present on the surface of the titanium-silicalite, to  $\text{Si-O-Si}(\text{R})_3$  groups which



are chemically inert to solvolysis of the epoxy ring.

The epoxidation reaction between the olefin and hydrogen peroxide is performed at a temperature of  
5 from about 0 to about 150°C. and at a pressure of from about 1 to about 100 atm with or without the presence of one or more solvents.

The epoxidation reaction may be performed in  
10 batch or in a continuous flow on a fixed bed, or in a CSTR reactor in a monophasic or biphasic system.

The catalyst is stable under the reaction conditions and may be completely recovered and reused.  
15 Examples of the solvents which can be used include polar compounds such as alcohols, ketones, esters, ethers, glycols, with the number of carbon atoms not too high, preferably less than or equal to 6 carbon atoms. Preferred examples of the alcohols are methanol and  
20 terbutanol. A preferred example of a ketone is acetone.

The olefinic compounds that may be epoxidized according to the present invention include compounds having the general formula:

25



30 wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may be the same or different and are selected from H and an alkyl, alkylaryl, cycloalkyl and alkylcycloalkyl group, wherein the alkyl group has from 1 to 20 carbon atoms, the alkylaryl group has from 7 to 20 carbon atoms, the cycloalkyl group has  
35 from 6 to 10 carbon atoms and the alkylcycloalkyl group

has from 7 to 20 carbon atoms. The  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  groups may be coupled together to form saturated or unsaturated rings (e.g.,  $R_1$ ,  $R_2$  may be coupled together and/or  $R_3$  and  $R_4$  may be coupled together).

5

The  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  groups described above may be substituted with at least one substituent selected from halogen (preferably Cl, Br and I), nitro, sulfonic, carbonilic, oxydrilic, carboxylic and ether  
10 groups. By way of example, the olefins that may be epoxidized in accordance with the present invention are, e.g., ethylene, propylene, allyl chloride, butene-2, butene-1, octene-1, 1-tridecene, mesityl oxide, isoprene, cyclooctene and cyclohexene and the like.

15

It is desirable to conduct the epoxidation reaction at a pressure higher than atmospheric pressure if gaseous olefins are used, in order to make them soluble or liquid under the reaction conditions.  
20 Operating at temperatures higher than 0°C. influences the kinetics of the reaction although the reaction proceeds rapidly even at temperatures near 0°C.

The following examples are directed to  
25 particular embodiments of the present invention. It should be noted, however, that the examples are merely illustrative and are not meant to limit the invention as set forth in the claims forming part of the application.

30

#### EXAMPLE 1

1154 g of tetraethylorthosilicate were added under strong stirring to 1232 g of a 12% by weight tetrapropylammonium hydroxide solution and heated for one hour at 60°C. 5049 g of demineralized water were  
35 added to the heated solution and stirring was continued

for another hour until a clear solution was obtained. 3000 g of titanium-silicalite was carefully slurried into the clear solution. The titanium-silicalite is prepared according to the method disclosed in European patent application 100119 incorporated herein by reference.

The resulting milky slurry was fed to a spray-dryer (Niro-Atomizer, disk-atomizer, inlet air temperature 300°C., outlet air temperature 120°C., chamber diameter 1.5m) obtaining dense microspheres having a mean diameter of about 20  $\mu$ m.

The atomized catalyst was put in a muffle and calcined for four hours at 550°C. 200 g of atomized titanium-silicalite thus prepared were slurried in 1 liter of distilled water containing 10 g of sodium acetate. The slurry was heated at reflux temperature for 10 minutes and then filtered. The aforementioned treatment was repeated a second time in the same way with the same reactants. The resulting product was filtered again and then washed many times with hot distilled water. Then the washed catalyst was dried in a stove and then in a muffle at 550°C.

#### EXAMPLE 2

150 g of titanium-silicate prepared in the same manner as in Example 1, were slurried in 500 ml of water containing 5 g of  $\text{Na}_2\text{HPO}_4$ . The slurry was heated at reflux temperature for 15 minutes. The heated slurry was filtered and the treatment was repeated a second time. Thereafter the resulting product was washed repeatedly as described in Example 1.

Similar dilute solutions using other bases may be employed in the same manner to prepare highly

active and selective epoxidation catalysts.

### EXAMPLE 3

195 g of distilled water, 280 g of methanol  
5 and 4.5 g of catalyst prepared as described in Example  
1, were loaded into a one liter steel autoclave provided  
with a mechanical stirrer, a thermostatic system and  
means for maintaining constant pressure. 56 g of a 32%  
by weight hydrogen peroxide solution were loaded in a  
10 tank connected to the autoclave. After thermostating at  
40°C. and pressurizing with propylene under stirring at  
6 atm (constant during the entire reaction), hydrogen  
peroxide was added in a single step to the slurry in the  
autoclave. Samples were taken at set time intervals and  
15 analyzed.

Hydrogen peroxide was titrated by iodometry  
and the reaction products were analyzed by gas  
chromatography, utilizing a column filled with Poropak  
20 PS, 1.8m long. The results are shown in Table 1.

### EXAMPLE 4

The procedure of Example 3 was followed using  
the same quantities of reactants, except that 4.5 g of the  
25 titanium-silicalite atomized as such without treatment with a base was  
used to carry out epoxidation of propylene. The results  
are shown in Table 1. As shown in Table 1, the results  
obtained using titanium-silicalite, without treatment with  
a base were not as good as those obtained with the base  
30 treated catalyst.

TABLE 1

t(min)	Example 3			Example 4		
	H <sub>2</sub> O <sub>2</sub> (M/Kg)	PO (M/Kg)*	Others (M/Kg)**	H <sub>2</sub> O <sub>2</sub> (M/Kg)	PO (M/Kg)*	Others (M/Kg)**
4'	0.744	0.245	0.001	0.661	0.320	0.007
12'	0.421	0.562	0.004	0.371	0.590	0.020
24'	0.225	0.757	0.008	0.185	0.753	0.052
40'	0.051	0.917	0.021	0.058	0.865	0.067

\*PO = Propylene oxide.

\*\*Propylene glycol, 1-methoxy-2-hydroxypropane, 2 methoxy-1-hydroxypropane.

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EXAMPLE 5

450 g of methanol, 100 g of octene-1, 5 g of catalyst prepared as in Example 2 were loaded in a 1 liter autoclave, provided with a mechanical stirrer, 5 thermostatic system and constant pressure control. 50 g of a 34% by weight solution of  $H_2O_2$  were loaded in the tank connected to the autoclave. After thermostating at 45°C., under strong stirring, hydrogen peroxide was added to the mixture of the other reactants. Samples 10 were drawn at regular time intervals and analyzed.

Hydrogen peroxide was determined through iodometry and the reaction products determined by gas liquid chromatography, after 1-hour of reaction time:

15	$H_2O_2$ Conversion	88%
	Octene Conversion	49.2%
	Selectivity to 1,2-epoxyoctane	98%

EXAMPLE 6

20 400 g of methanol, 100 g of allyl chloride, 10 g of catalyst prepared as in Example 1, were put in an autoclave as in Example 5. 70 g of a 34% by weight solution of  $H_2O_2$  were loaded into the tank. The reaction was carried out at 60°C. for 30 minutes. 25 Hydrogen peroxide and allyl chloride conversion and selectivity to epichlorohydrin was measured in the same general manner described in Example 5.

	$H_2O_2$ Conversion	93%
	Allyl Chloride Conversion	49.7%
30	Selectivity to Epichlorohydrin	97.5%

EXAMPLE 7

21 g of titanium-silicalite prepared in the same manner as in Example 1, calcined at 550°C. and cooled in 35 a dry atmosphere, were slurried in a mixture of 20 cc of

anhydrous pyridine, 9 cc of trimethylchlorosilane and 3 cc of hexamethyldisilazane. The slurry was kept under stirring at 50°C. for 2 hours. The solid was then filtered, washed twice with 10 cc of anhydrous pyridine, twice with 10 cc of acetonitrile, three times with 10 cc of water and then thoroughly dried in vacuo.

#### EXAMPLE 8

1154 g of tetraethylorthosilicate were added under strong stirring to 1232 g of a 12% by weight solution of tetrapropylammonium hydroxide and heated for 1 hour at 60°C. 5049 g of demineralized water were then added to the heated mixture and stirring was maintained for another hour to thereby obtain a clear solution. 3000 g of titanium-silicate, prepared according to Example 1 were carefully slurried into the clear solution.

The resulting milky slurry was fed to a spray-dryer (Niro Atomizer, disk atomizer; inlet air temperature 300°C.; outlet air temperature 120°C.; chamber diameter 1.5 m) obtaining dense microspheres having a mean diameter of about 20  $\mu$ m.

The atomized catalyst was put in a muffle and calcined for four hours at 550°C. 12g of the resulting titanium-silicate thus prepared were treated at 80°C. with 6 cc of bis(trimethylsilyl)acetamide in 10 cc of anhydrous acetonitrile for 2 hours.

The thus obtained solid product was filtered, washed many times with hot acetonitrile, and then methanol. The washed product was dried in a stove at 100°C.

#### EXAMPLE 9

In a similar manner as described in Example 8,

10 g of titanium-silicate was treated with 3 cc of hexamethyldisilazane in 10 cc of acetonitrile. After refluxing for 2 hours, the resulting product was filtered, washed many times with acetonitrile and finally washed three times with water. The washed product was then dried in vacuo.

#### EXAMPLE 10

190 g of distilled water, 280 g of methanol and 4.5 g of titanium-silicalite were loaded into a 1 liter steel autoclave, provided with a mechanical stirrer, thermostatic system and constant pressure control. 52 g of a 34% by weight solution of hydrogen peroxide were loaded in a tank connected to the autoclave.

After thermostating at 40°C. and pressuring with propylene, under stirring, at a constant pressure of 6 atm, the entire amount of hydrogen peroxide was added in a single step to the contents of the autoclave. Samples were drawn at regular intervals and analyzed. Hydrogen peroxide was titrated by iodometry and the reaction products were analyzed by gas-liquid chromatography on a column filled with Poropak PS, 1.8 m long. The results are shown in Table 2.

#### EXAMPLE 11

A test was carried out in the same way and with the same reactants as those in Example 10, except that 4.5 g of titanium-silicalite treated in the same manner as Example 7 were loaded into the autoclave. The results are shown in Table 2. As shown in Table 2, the selectivity to the desired epoxide was significantly greater than the selectivity using the untreated catalyst described in Example 10.



Example 10Example 11

t(min)	H <sub>2</sub> O <sub>2</sub> (M/Kg)	PO (M/Kg)*	Others (M/Kg)**	H <sub>2</sub> O <sub>2</sub> (M/Kg)	PO (M/Kg)*	Others (M/Kg)
4'	0.660	0.320	0.006	0.783	0.208	0.002
12'	0.371	0.590	0.020	0.481	0.503	0.008
24'	0.186	0.753	0.054	0.235	0.747	0.009
40'	0.058	0.865	0.067	0.089	0.881	0.020

\*PO = Propylene oxide.

\*\*Propylene glycol, 1-methoxy-2-hydroxypropane, 2 methoxy-1-hydroxypropane.

EXAMPLE 12

450 g of methanol, 100 g of octene-1, and 5 g of catalyst prepared as in Example 8, were loaded into a one liter autoclave, provided with a mechanical stirrer and a thermostatic system and a constant pressure control. 50 g of a 34% by weight solution of  $H_2O_2$  were loaded in a tank connected to the autoclave. After thermostating at 45°C. under strong stirring, hydrogen peroxide was added to the mixture of the other reactants. Samples were drawn at regular intervals and analyzed.

Hydrogen peroxide was titrated by iodometry and the reaction products analyzed by gas-liquid chromatography after one hour.

$H_2O_2$ Conversion	85%
Octene Conversion	47.5%
Selectivity to 1,2 epoxyoctane	97.5%

EXAMPLE 13

The reaction was carried out in the same manner and with the same equipment as described in Example 12. 400 g of methanol, 100 g of allyl chloride, and 10 g of the catalyst prepared as in Example 9 were added to the autoclave. 70 g of a 34% by weight solution of  $H_2O_2$  were loaded in the tank. The reaction was carried out at 60°C. for 30 minutes.

$H_2O_2$ Conversion	94%
Allylchloride Conversion	50.1%
Selectivity to Epichlorohydrin	98%

CLAIMS

- 1) A process for the epoxydation of olefinic compounds comprising reacting in a reaction zone one or more olefinic compounds with hydrogen peroxide introduced as such or produced by substances which can produce it at the reaction conditions, in presence of a synthetic zeolite as catalyst, containing titanium atoms corresponding to the general formula  $x \text{TiO}_2 \cdot (1-x) \text{SiO}_2$  wherein  $x$  is in the range of from 0.0001 to 0.04 and titanium vicariates silicon, characterized in that the catalyst is neutralized, as to its acidity, with neutralizing agents.
- 2) A process according to claim 1 characterized in that neutralization may occur before and/or during the reaction.
- 3) A process according to claim 2 characterized in that when neutralization occurs before and/or during the reaction, the neutralizing agents are basic substances which are, at least, hydrosoluble.
- 4) A process according to claim 3 characterized in that the basic substances are strong bases.

- 5) A process according to claim 4 characterized in that the strong bases are NaOH or KOH.
- 6) A process according to claim 3 characterized in that the basic substances are weak bases.
- 5 7) A process according to claim 6 characterized in that the weak bases are chosen among  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{KHCO}_3$ ,  $\text{LiHCO}_3$ ,  $\text{K}_2\text{HPO}_4$ , alkaline and/or alkaline earth salts of carboxylic acids with a number of carbon atoms from 1 to 10 and alkaline and/or alkaline-earth alcoholates with a number of carbon atoms from 1 to 10.
- 10
- 8) A process according to Claim 2 characterized in that when neutralization occurs before the reaction, the neutralizing agents are compounds of the type
- 15
- $\text{X-Si-(R)}_3$  where X is Cl, Br, I,  $\text{CH}_3\text{CON-Si-(CH}_3)_3$ ,  $\text{CF}_3\text{COON-Si-(CH}_3)_3$ ,  $\text{R}_3\text{SiNH}$ , imidazolyl, and R is an alkyl, aryl, alkylaryl group wherein the alkyl has a number of carbon atoms from 1 to 4.
- 20
- 9) A process according to claim 8 characterized in that neutralization occurs by reacting
- 25 the compounds of said general formula with

the catalyst in an inert solvent.

10) A process according to claim 9 characterized  
in that the inert solvent is chosen among  
acetonitrile, chloroform, pyridine, dioxane,  
5 eventually in presence of an organic base.

11) A process according to claim 10  
characterized in that the organic base is  
chosen among pyridine and tertiary amines.

12) A catalyst, for the epoxydation of olefines,  
10 which is constituted by a synthetic zeolite  
containing titanium atoms corresponding to  
the general formula  $x\text{TiO}_2 \cdot (1-x) \text{SiO}_2$   
wherein x is in the range of from 0.0001 to  
0.04 and titanium vicariates silicon,  
15 characterized in that the surface of the  
catalyst has Si-O-Si ( $\text{R}_3$ ) groups, R is  
selected from alkyl, aryl, and alkylaryl  
wherein the alkyl group has from 1 to 4  
carbon atoms, and said surface has  
20 substantially no SiOH groups. ,